REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
20/11/2014	Final Report	August 15 2011- August 15 2014

4. TITLE AND SUBTITLE

INTEGRATION OF NATURAL POLYMERS AND SYNTHETIC NANOSTRUCTURES

5a. CONTRACT NUMBER

5b. GRANT NUMBER

FA9550-11-1-0233

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Vladimir V. Tsukruk

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Georgia Tech Research Corporation
505 10st NW, Atlanta GA 30332

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

USAF, Air Force Office of Scientific Research
875 N. Randolph St, Room 3112
Arlington VA 22203

10. SPONSOR/MONITOR'S ACRONYM(S)

AFOSR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The overall goal of this project is to develop a fundamental understanding of critical material interfaces in naturally occurring materials in order to provide assembly strategies for the development of high-performance functional nanocomposites. The general strategy is to study the assembly process at critical interfaces that dramatically influence the dispersion of nanofillers, the interfacial interactions between matrix and nanofiller, and ultimately the performance of nanocomposites. Specifically, our research plan is focused on the understanding of the fundamental mechanisms of self-assembly in silk biopolymers and their interfacial interactions with inorganic nanostructures. We employ fabrication techniques including layer-by-layer (LbL) deposition, vacuum-assisted self-assembly, and spin-assisted self-assembly, as well as patterning techniques including capillary transfer lithography and solvent-assisted micro-contact molding to create complex silk structures and nanocomposites. We demonstrated fabrication of ultrastrong and tough biographene paper with potential for conductive path writing.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	UU		**19b. TELEPHONE NUMBER** *(include area code)*
U	U	U			

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

Final Performance Report
August 2011 - August 2014
FA9550-11-1-0233: INTEGRATION OF NATURAL POLYMERS AND SYNTHETIC NANOSTRUCTURES

PI: Vladimir V. Tsukruk
School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Dr., NW, Atlanta, GA 30332-0245; Ph.: 404-894-6081; vladimir@mse.gatech.edu ; http://polysurf.mse.gatech.edu/

Project objectives

The overall goal of this project is to develop a fundamental understanding of critical material interfaces in *naturally* occurring materials in order to provide assembly strategies for the development of high-performance functional nanocomposites. The general strategy is to study the assembly process at critical interfaces that dramatically influence the dispersion of nanofillers, the interfacial interactions between matrix and nanofiller, and ultimately the performance of nanocomposites.

Specifically, our research plan is focused on the understanding of the fundamental mechanisms of self-assembly in silk biopolymers and their interfacial interactions with inorganic nanostructures. We employ fabrication techniques including layer-by-layer (LbL) deposition, vacuum-assisted self-assembly, and spin-assisted self-assembly, as well as patterning techniques including capillary transfer lithography and solvent-assisted micro-contact molding to create complex silk structures and nanocomposites. We extensively characterize the structure, morphology, and properties of these materials with respect to their processing conditions, spatial confinement, interfacial conditions and interactions, as well as external stimuli such as pH.

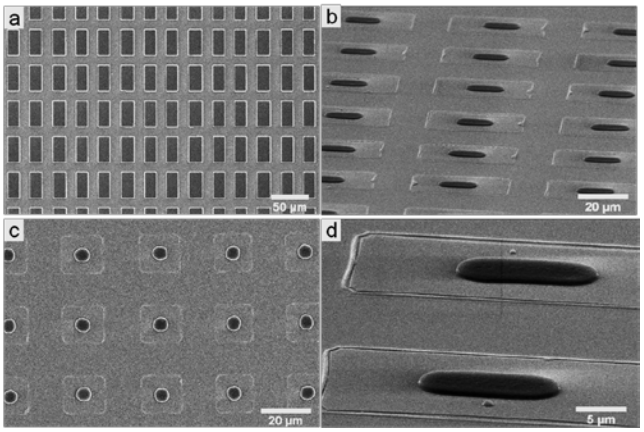
This cross-disciplinary project will enhance the collaboration with our partners from academic, national and AFRL, WPAFB (Naik, Bunning, Vaia, Kelley-Loughnane, and Stone). The collaboration with the AFRL groups such as sample exchange, complementary characterization, synthesis on new biomaterials, and interface/surface modification will be facilitated by mutual visits, student exchanges, joint student supervision, student summer internships at AFRL, joint presentations and publications, joint patent filing, and the mutual transfer of technologies relevant to long-term fundamental research interests at USAF. Two students graduated from PI's group joined AFRL as researchers.

Ongoing collaboration with three academic labs will bring biomolecules to the PI lab such as silk fibroin (D. Kaplan, Bioengineering Department, Tufts) and engineered silk (T. Scheibel, U. Bayreuth). The proximity of ORNL and initiated contacts with Dr. J. Anker facilitate the availability of this neutron source with the highest flux for unique measurements.

Students participating in the project constantly interact with researches at AFRL by numerous means including joint supervision and GT-AFRL summer internships. They will mature as multifaceted researchers deeply involved into USAF-relevant fundamental studies in highly multidisciplinary fields of biotechnology, materials science, nanotechnology, and biochemistry. The synergism of joint collaborative efforts of the PI group and highly skilled AFRL research groups will offer invaluable experience to graduate students and enhance a prospective workforce training for the USAF.

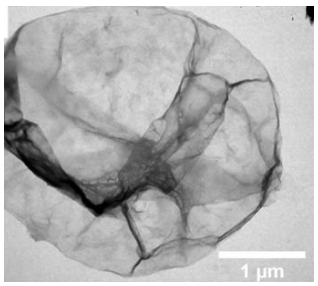
Summary of Major Results:

Silk ultrathin coatings as active nanomaterials. We demonstrate the fabrication of ordered arrays of self-encapsulated "micro-bubble" materials constructs based on the capillary-driven collapse of flexible silk fibroin sheets during frontal dissolution of the encapsulated material (Figure). The individual micro-bubbles of different shapes are composed of a sacrificial substrate material (any dissolvable polymeric or biopolymeric materials) encapsulated within the ultrathin silk coating, which covers and seals the inner material during dissolution of supporting layer. The array of microscopic rectangular multi-layer silk sheets on supporting polymer layers can be selectively dissolved along the edges to initiates their self-encapsulation. The resulting micro-bubble morphology, shape, and arrangements can be readily pre-programmed by controlling the geometry of the silk sheets, such as thickness, dimension, and the aspect ratio. We demonstrated that these micro-bubble constructs can be utilized for encapsulation of various materials as well as nanoparticles in a single or multi compartmental manner. The highly ordered array of micro-bubbles and the "sandwich" constructions enable pre-programmed encapsulation and co-encapsulation of different materials in multicompartmental constructs, which presents a promising platform for the formation of ordered addressable arrays of robust microcontainers for spatial and timely encapsulation and release systems.

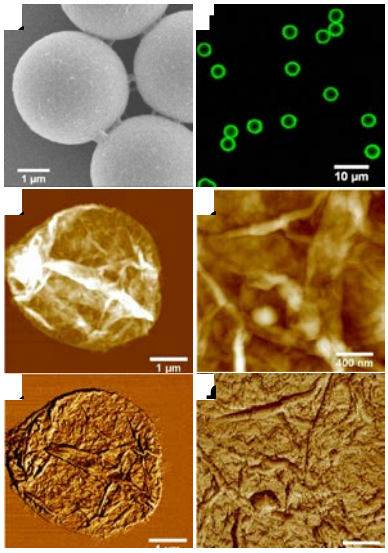


Patterned encapsulation of substrate material with "grabbing" silk bimorph coatings

We demonstrated dramatically reinforced silk microcapsules with graphene oxide flakes by the assembly of robust and stable microcapsules from poly-amino acid modified silk fibroin reinforced with graphene oxide flakes using layer-by-layer (LbL) assembly which are based on biocompatible natural protein and carbon nanosheets (Figure). The composite microcapsules are extremely stable in acidic (pH 2.0) and basic (pH 11.5) conditions accompanied with pH-triggered permeability, which facilitated the controllable encapsulation and release of macromolecules. The graphene oxide incorporated into ultrathin LbL shells induced greatly reinforced mechanical properties, with an elastic modulus which is two orders of magnitude higher than the typical values of original silk LbL shells and accompanied by significant, three-fold reduction in a pore size. These nanocomposite microcapsules possessed dramatically increased elastic moduli of about 0.5 GPa (as compared to about 2 MPa for pure silk microcapsules) and reduced permeability with pores size down to 11 nm (from about 32 nm pores in purely silk microcapsules), due to the



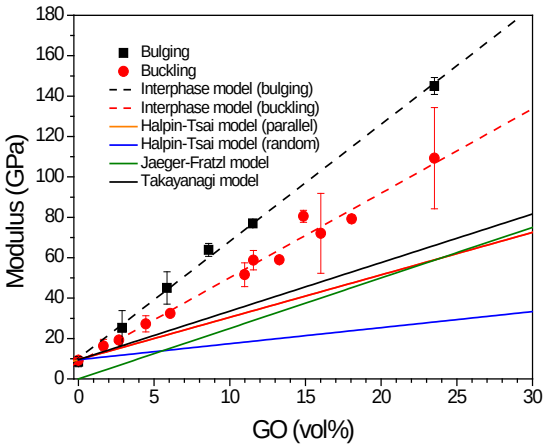
The TEM image of graphene oxide-silk ionomer microcapsule



Reinforced graphene oxide-silk microcapsules: initial cores, confocal image after core release, and AFM images of collapsed microcapsules.

presence of strong, flexible, and overlapped graphene oxide flakes within soft silk shells. Such strong nanocomposite microcapsules can provide solid protection of encapsulated cargo under harsh conditions, indicating a promising candidate with controllable loading/unloading for drug delivery, reinforcement and bioengineering applications.

Ultra-robust graphene oxide reinforced silk fibroin nanocomposites by interphase reinforcement. Reconstituted silk fibroin from *Bombyx Mori* silkworm silks is an mass-production available source of the excellent biopolymeric material that is strong, transparent, biocompatible, and biodegradable. Ultrathin (<100 nm) films of silk fibroin or its nanocomposites fabricated by either drop casting or spin-assisted layer-by-layer (SA-LbL) techniques are not comparable to natural silk fibers in terms of mechanical properties, mainly because the losing of the hierarchical nanostructures that induced by the biological spinning process. We dramatically reinforced the mechanical properties of the SA-LbL silk fibroin nanomembranes by employing graphene oxide as a strong nanofiller between the layers of silk fibroin molecules.

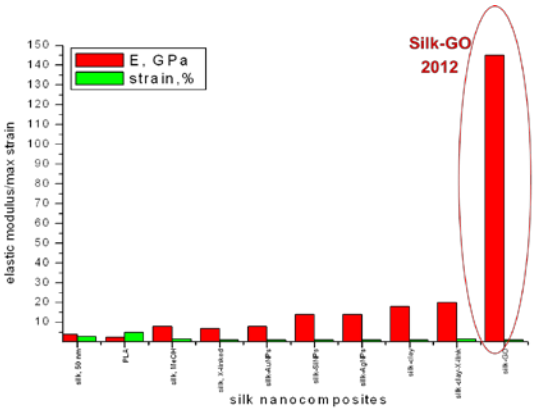


The Young's moduli of the nanocomposites with different graphene oxide contents compared with the values predicted by the theoretical models.

After the addition of graphene oxide, the Young's modulus of the silk membrane subjected to tensile stress (bulging tests) increased linearly with the graphene oxide concentration, eventually reaching the highest value of around 150 GPa. The compressive elastic modulus (buckling tests) also increases linearly but is slightly lower than the tensile modulus for the same graphene oxide content. The outstanding value of tensile modulus is by far the highest modulus recorded for nanocomposite biopolymer membranes without the expense of very high filler concentration. Moreover, it is even more surprising to find that the experimental values are ***systematically and significantly higher than the theoretical values*** predicted by Halpin-Tsai laminated model for perfect orientation of 2D reinforcing sheets as well as other mechanical models.

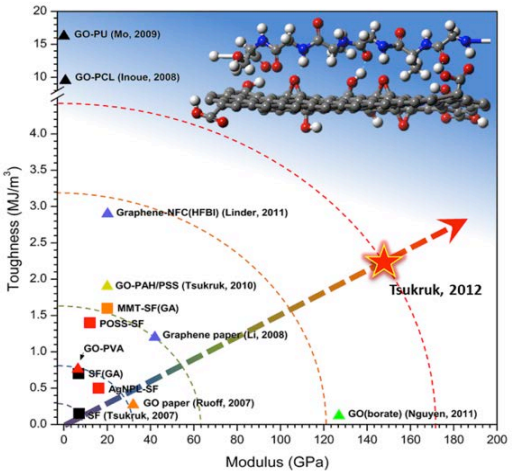
To understand this phenomenon, we considered the possibility of a unique interphase reinforcement mechanism in nanocomposites based upon the formation of ***molecular interphase zones between two components***. In order to determine the thickness of the interphase and the extent of the corresponding reinforcing phenomenon, we developed a mechanistic model of interphase reinforcement. In this model, we assumed that the elastic modulus varies monotonically along the normal direction within the interphase zone and the rate of the decay depends on the local modulus and the total percentage of decay similar to those suggested for layered nanocomposites.

Finally, the analysis of all data on mechanical strengths collected in the previous AFOSR project and in literature for nanocomposites from silk materials reinforced with different nanostructures such as nanoparticles, clay, nanoplatelets, or with covalent crosslinking shows that the value on the ***elastic modulus obtained in the current project is superior to anything reported to date***. The elongation to break remained around 1% indicating no excessive brittleness of these outstanding biopolymer nanocomposites (Figure). This intriguing discovery is the base for future research activities.



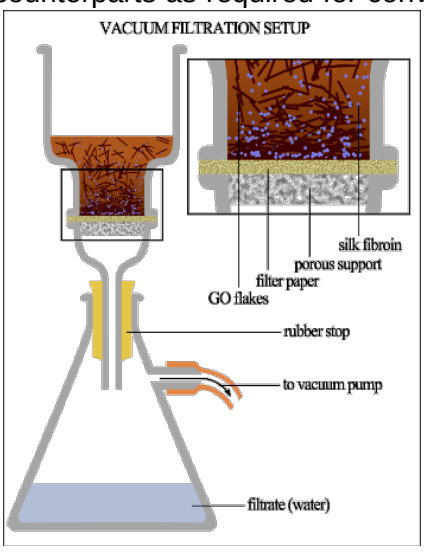
The elastic modulus and max strain of the representative soft materials and silk fibroin incorporated nanocomposite materials.

The synergistic enhancement of heterogeneous graphene oxide and silk components with complementary nature of interfacial bonding resulted in ***ultrastrong interphase nanocomposites (figure)*** with 50-150 GPa tensile modulus without compromising flexibility, which is by far the highest reported value for silk-based nanocomposites (both ultrathin (100 nm) and thin (several microns) have been fabricated). The ultimate strength of the nanomembranes has also increased by at least four folds to over 300 MPa. The model of interphase reinforcement shows excellent match with experimental data for the thickness of the interphase zone of about 1 nm that is close to the backbone diameter of spread silk macromolecules "arrested" by the heterogeneous surface of graphene oxide sheets. The enhanced mechanical properties of the GO-SF nanocomposite membranes which are much better than anything reported to date (Figure) are potentially useful in nanosensors, microencapsulation, and protective coatings.



Literature results for toughness and modulus for graphene nanocomposites in comparison with our result.

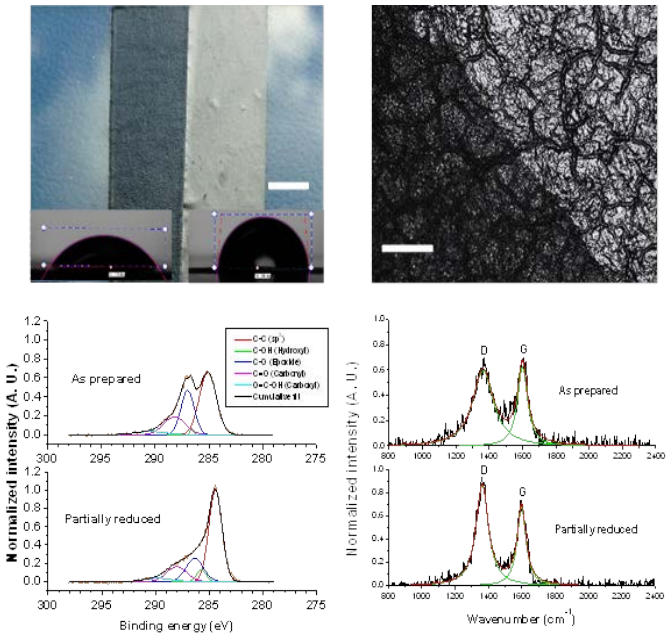
One-pot laminate nanocomposites from silk and graphene oxide. We applied a *one-pot vacuum-assisted assembly from homogeneous mixed solution of graphene oxide and silk*. The proposed method is based on the unique silk ability to self-assembly without oppositely-charged counterparts as required for conventional LbL assembly. We anticipate that one-pot mixing will provide a unique route to overcome major obstacles for developing laminated structures and to realize the potentials for high-performance nanocomposites. This method affords improved solubility and compatibility of the silk and inorganic materials and, therefore, may result in highly homogeneous materials, a critical challenge in case of conventional LbL assemblies. On the other hand, it gives an opportunity to obtain well-defined and stratified films with precisely designed laminated morphology, structure, and composition at the nanoscale level, which cannot be accomplished when casting solution mixtures.



Experimental setup of the vacuum-assisted filtration system.

In this preliminary experiment, the as prepared paper was sandwiched between two pieces of thin aluminum foils under mild pressure. The chemical reduction can proceed efficiently with as high as 15 wt% of silk fibroin intercalated in the graphene oxide structure with all changes observed (contact angle, XPS, Raman, and SEM) indicating high

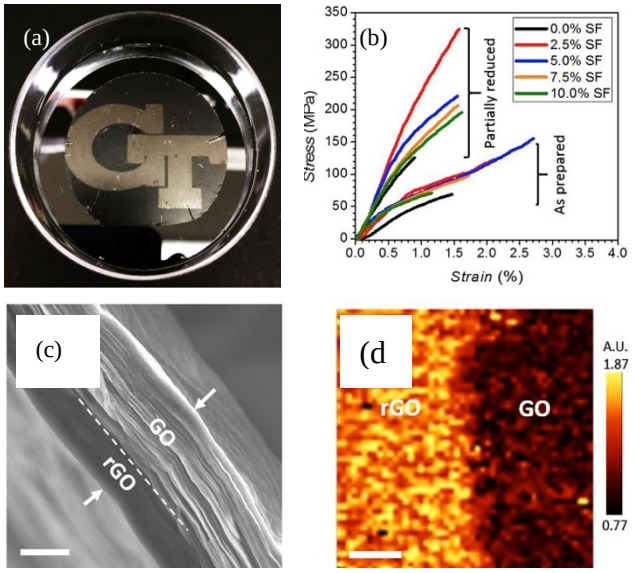
reduction of the initial paper and metal-like properties of reduced areas. It is important to note that although acidic conditions facilitate the efficient reduction of graphene oxide, the chemical reaction can be conducted in neutral condition at pH 7 and room temperature.



Characteristics of GO-SF paper before and after selective reduction. (a) Micrographs (scale bar: 5 mm) of two strips of graphene oxide paper before (left) and after (right) reduction and their contact angles (inset). (b) Reflective optical micrograph showing the border (scale bar: 200 μm). XPS C1s high resolution spectra (c), and Raman spectra (d) of the graphene oxide paper before and after selective reduction.

Eco-friendly and high-resolution reduction of GO biographene papers. By utilizing the favorable heterogeneous binding theory established in the previous study (section above), we replaced traditional synthetic binders in GO papers with universal ***biopolymer "binder"-silk fibroin***. The fabrication of GO-SF microfilms using vacuum-assisted self-assembly (VA-SA) is faster and readily for scaling up in contrast to the SA-LbL technique. The mechanical properties of the GO-SF microfilms are significantly improved by intercalating different amount of silk fibroin molecules (0.5-10 wt%). Small amount of SF intercalation resulted in excellent mechanical properties, including 300 MPa ultimate strength, 2.5% ultimate strain, and 2.6 MJ m^{-3} toughness.

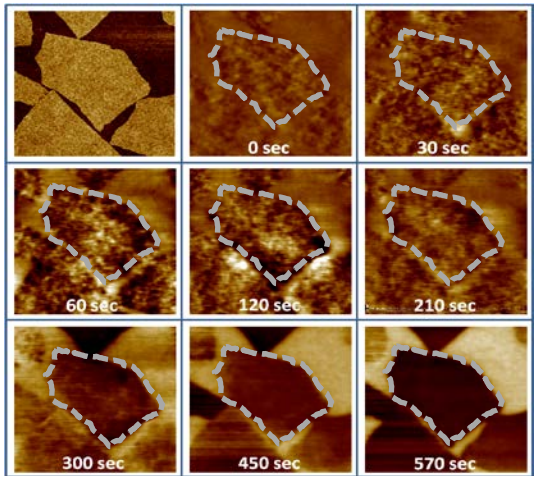
We also report a novel way for facile writing-in of electrically conductive microscopic patterns (conductivity about 2000 S m^{-1}) by *a* ***localized electrochemical reduction*** *with micron-scale resolution* of such robust bio-graphene laminated papers with enhanced toughness. Aluminum metal foils have been introduced as an active reducing agent to remove the insulation-inducing epoxide oxygens from graphene oxide. The through-thickness reduction can be well controlled by adjusting the reduction time or reaction parameters. This 3-D electrochemical microstamping writing-in approach can be valuable for future inexpensive, disposable, biodegradable paper with written electrical circuitries integrated into biolelectronic, flexible, and conformal devices.



Patterned biographene paper, mechanical properties, laminated morphology, and Raman mapping at boundary between graphene oxide-graphene regions.

Mapping surface functionalities of GO by EFM. We report using the electrostatic force microscopy (EFM) the first example of continuous monitoring of the evolution of heterogeneous distribution of oxygenated functionalities on the entire surface of the individual

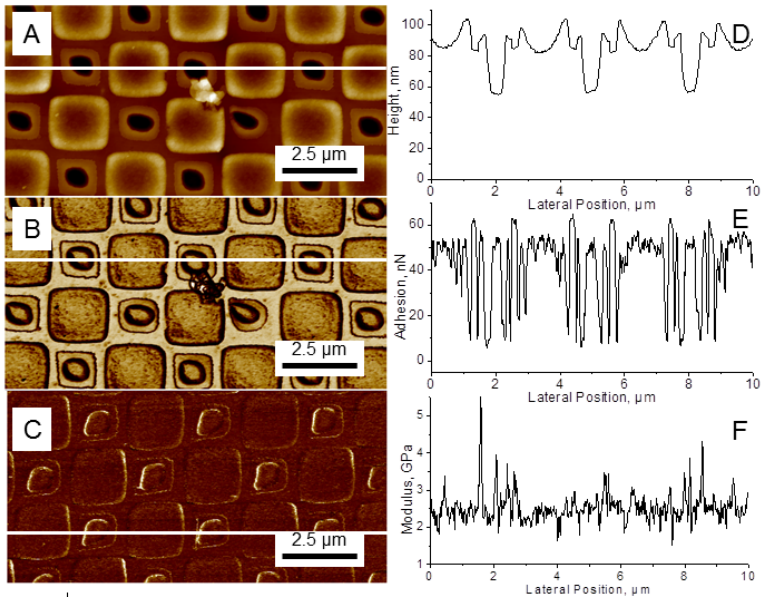
graphene oxide flakes during chemical reduction process. Quantitative analysis of the EFM images revealed the heavily oxidized surface areas with randomized nanoscale domains of 50-100 nm across. These domains cover around 60% of the graphene oxide surface and are negatively charged with a lower surface potential than the corresponding graphitic domains with respect to the doped silicon tip.



EFM images of gradually reducing graphene oxide flake to conducting graphene flake (the same flake) with chemical reduction.

The charge densities over the graphene oxide surface with a mixed concentration of oxidized and graphitic areas were mapped with nanoscale resolution and the localized oxidization level was evaluated for the same microscopic flake in step-by-step chemical reduction process (Figure). The results suggested complex oxidizing process affecting differently graphene oxide-air and graphene oxide-solid interfaces. The non-destructive monitoring of the evolution of the heterogeneous charge distribution over the surface of the individual graphene oxide flakes will provide fundamental physiochemical information for designing reliable graphene-based structures, devices, and composites.

Patterning Thin Films of Recombinant Spider Silk Proteins. Recombinant spider silk proteins mimicking the properties of dragline silk proteins represent a class of materials which hold great potential for future high performance applications. Here we explore the self-assembly behavior of a recombinantly produced spider silk protein based on the dragline silk of the *A. diadematus*, eADF4 (C16), by selectively patterning its secondary structure using capillary transfer lithography (CTL) and solvent-assisted micro-contact molding (SAMIM) (Figure).

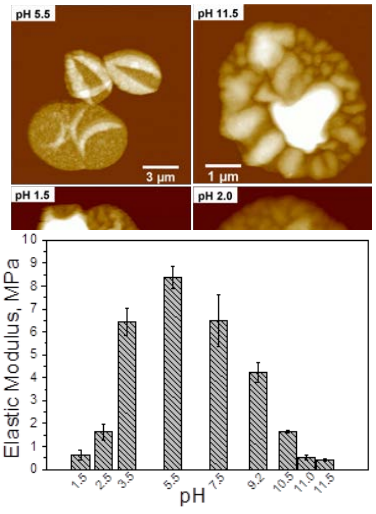


Two conformational transitions were observed, influenced by initial solvent composition: α-helix/random coil conformation to silk II conformation (by casting from 1,1,1,3,3,3-hexafluoro-propanol, HFIP) and moderate initial β-sheet content to silk II conformation (casting from formic acid, FA). For CTL, patterns included 7 micrometer PS lines separated by 3 micrometer spaces and a checkerboard pattern of 1.5 micrometer by 1.5 micrometer PS squares. Furthermore, by using the SAMIM technique, we were able to achieve a sub-micron pattern resolution of approximately 400 nm PS lines separated by 300 nm spaces.

The patterned films were characterized by atomic force microscopy. Significant differences in the tip-sample adhesive interaction forces were observed between the masked and unmasked

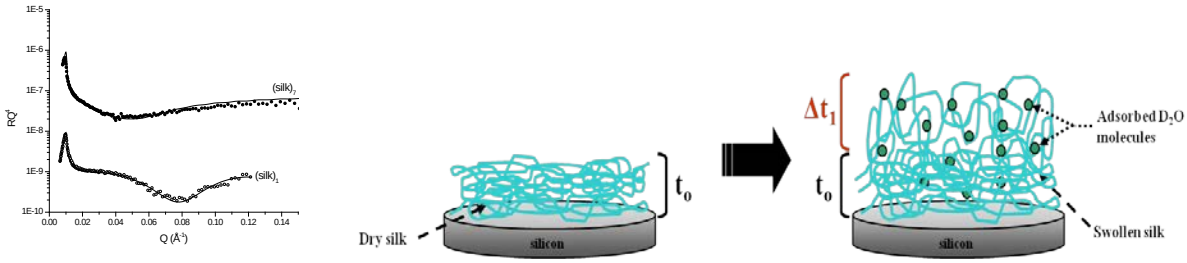
regions in C16 films cast from HFIP. However, no such difference was observed for those films cast from FA. Additionally the elastic modulus for all patterned films appeared to be uniform at about 2-4 GPa.

Permeability and Micromechanical Properties of Silk Ionomer Microcapsules. We studied pH-responsive behavior of the layer-by-layer (LbL) microcapsules fabricated from silk fibroin chemically modified with different poly-amino acid side chains: cationic (silk-poly L-lysine, SF-PL) or anionic (silk-poly-L-glutamic acid, SF-PG) (Figure). We observed that stable ultrathin shell microcapsules can be assembled with dramatic increase in swelling, thickness and microroughness at extremely acidic (pH<2.5) and basic (pH>11.0) conditions without noticeable disintegration. These changes are accompanied dramatic changes in shell permeability with a two orders of magnitude increase in the diffusion coefficient.



Moreover, the silk ionomer shells undergo remarkable softening with a drop in Young's modulus by more than an order of magnitude due to the swelling, stretching, and increase in material porosity. The ability to control permeability and mechanical properties in a wide range for the silk-based microcapsules, with distinguishing stability under harsh environmental conditions, provides an important system for controlled loading and release-related applications.

Silk surface layers morphology from neutron reflectivity. Neutron reflectivity (NR) measurements of ultrathin surface films (below 30 nm) composed of *Bombyx mori* silk fibroin protein were used to obtain internal structure in both dry and swollen states. Reconstituted aqueous silk solution deposited on a silicon substrate using the SA-LbL technique resulted in a monolayer silk film with constant scattering length density (SLD) for single layer deposition. However, a vertically segregated ordering with two different regions has been observed in dry, thicker, seven-layer silk films. The vertical segregation of silk multilayer films indicates the presence of a different secondary structure of silk in direct contact with the silicon oxide surface (first 6 nm).



Examples of neutron reflectivity data with fits for two silk films (left) and schematic of the two-tier swollen morphology of ultrathin silk ultrathin films where the t_o region indicates interfacial segregated silk II phase, and Δt_1 represent the swollen region of random coil silk and trapped air bubbles (right).

The layered structure can be attributed to interfacial β-sheet crystallization for the initially deposited silk surface layers with the preservation of less dense, random coil secondary structure for the layers that follow. This segregated structure of solid silk films defines their complex non-uniform swelling behaviour. For a silk monolayer with an initial thickness of 6 nm,

the non-uniform swelling resulted in the formation of two-tier swollen layering regime at the D_2O-film interface while thicker silk film undergo delamination during swelling.

Finally, in ***several invited reviews*** we summarized state-of-the-art developments in the fields of nanocomposite materials with integrated natural monomers/polymer and synthetic components: plasma polymerized polyaminoacid ultrathin films and coatings responsive hybrid natural and polymeric nanomaterials and graphene-polymer-biopolymer nanocomposite. These reviews included our recent and previous results accumulated in the current as well as prior AFOSR projects.

Books and review articles (2012-2014):

1. V. V. Tsukruk, S. Singamaneni, ***Scanning Probe Microscopy of Soft Matter: Fundamentals and Practices,*** Wiley-VCH, Weinheim, **2012**, 661 pages.
2. K. Hu, D. D. Kulkarni, I. Choi, V. V. Tsukruk, Graphene–Polymer Nanocomposites for Structural and Functional Applications, *Prog. Polym. Sci*., **2014**, *39*, 1934-1972.
3. I. Drachuk, M. K. Gupta, V. V. Tsukruk, Biomimetic coatings to control cellular function through cell surface engineering, *Adv. Funct. Mater.,* **2013,** *23,* 4437-4453.
4. M. C. Vasudev, K. D. Anderson, V. V. Tsukruk, T. J. Bunning, R. R. Naik, Exploration of Plasma-Enhanced Chemical Vapor Deposition as a Method for Thin Film Fabrication with Biological Applications, *ACS Appl. Mater. Interfaces*, **2013,** *5,* 3983-3994.

Peer-reviewed project publications:

1. D. D. Kulkarni, S. Kim, M. Chyasnavichyus, K. Hu, A. G. Fedorov, V. V. Tsukruk, Chemical Reduction of Individual Graphene Oxide Sheets as Revealed by Electrostatic Force Microscopy, *J. Am. Chem. Soc.,* **2014,** *136,* 6546-6549.
2. C. Ye, D. D. Kulkarni, H. Dai, V. V. Tsukruk, Programmable Arrays of “Micro-bubble” Constructs via Self-Encapsulation, *Adv. Funct. Mater.,* **2014**, *24*, 4364-4373.
3. R. Suntivich, I. Drachuk, R. Calabrese, D. L. Kaplan, V. V. Tsukruk, Inkjet printing of silk nest arrays for cell hosting, *Biomacromolecules*, **2014,** *15,* 1428-1435.
4. K. Hu, L. S. Tolentino, D. D. Kulkarni, C. Ye, S. Kumar, V. V. Tsukruk, Written-in Conductive Patterns on Robust Graphene Oxide Biopaper by Electrochemical Microstamping, *Angew. Chem.,* **2013,** *52,* 13784-13788.
5. K. Hu, M. K. Gupta, D. D. Kulkarni, V. V. Tsukruk, Ultra-Robust Graphene Oxide-Silk Fibroin Nanocomposite Membranes, *Adv. Mater.*, **2013**, *25,* 2301-2307.
6. Drachuk, I., O. Shchepelina, S. Harbaugh, N. Kelley-Loughnane, M. Stone, V. V. Tsukruk, Cell Surface Engineering with Edible Protein Nanoshells, *Small,* **2013**, *9,* 3128-3137.
7. M. K. Gupta, D. D. Kulkarni, R. Geryak, S. Naik, V. V. Tsukruk, A robust and facile approach to assembling mobile and highly-open unfrustrated triangular lattices from ferromagnetic nanorods. *Nano Lett.*, **2013**, *13,* 36-42.
8. B. Wallet, E. Kharlampieva, K. Campbell-Proszowska, V. Kozlovskaya, S. Malak, J. F. Ankner, D. L. Kaplan, V. V. Tsukruk, Silk Layering as Studied with Neutron Reflectivity, *Langmuir,* **2012,** *28*, 11481−11489
9. C. Ye, I. Drachuk, R. Calabrese, H. Dai, D. L. Kaplan, V. V. Tsukruk, Permeability and Micromechanical Properties of Silk Ionomer Microcapsules, *Langmuir,* **2012,** *28*, 12235−12244
10. S. L. Young, M. Gupta, C. Hanske, A. Fery, T. Scheibel, V. V. Tsukruk, Utilizing Conformational Changes for Patterning Thin Films of Recombinant Spider Silk Proteins, *Biomacromolecules,* **2012,** *13,* 3189-3199.

11. K. D. Anderson, S. L. Young, H. Jiang, R. Jakubiak, T. J. Bunning, R. R. Naik, V. V. Tsukruk, Plasma Enhanced Co-Polymerization of Amino Acid and Synthetic Monomers, *Langmuir*, **2012,** *28,* 1833-1845.

30+ presentations have been delivered in USA, Europe, and Asia by the PI and his students at professional conferences and seminars.

Provisional patent application GTRC ID 6627, K. Hu, V. V. Tsukruk, Written-in Conductive Patterns on Robust Graphene Oxide Biopaper by Electrochemical Microstamping, 2014

Personnel training and collaboration with AFRL researchers

MSE graduate students, who participated and were fully or partially supported by the project in 2012-2014 are: P, Zackowski, S. Young, K. Hu, C. Ye, I. Drachuk (graduated in 2014, currently at AFRL), M. Gupta (graduated in 2012, currently at AFRL) and K. Anderson (graduated in August 2012, currently at Dow Chemical), all are involved in close collaboration with Tufts, UBayreuth, and AFRL researchers. Three students (Drachuk, Anderson and Gupta) are co-advised by AFRL researchers (Kelley, Bunning and Naik) and conducted summer research at AFRL to enhance collaboration. In the course of the project, the students were involved in fruitful collaboration with Kaplan (Tufts) and Scheibel (UBayreuth) research groups and with AFRL researchers (Naik's, Kelley's, and Bunning's groups).

Honors, fellowships, and professional services relevant to the project

Students:

- Irina Drachuk, 2014, NRC post-doctoral Fellow at AFRL
- Irina Drachuk, 2014, ACS Graduate Student Award Symposium
- Maneesh Gupta, 2013 IC post-doctoral Fellowship at Princeton
- Kesong Hu, 2013, 2014 best poster MSE Awards in Soft Materials
- Irina Drachuk, 2013 best poster MSE Award in Biomaterials

PI (new only):

- Fellow, American Chemical Society, 2014
- Member, Editorial Board, *ACS Biomaterials,* 2014-present
- Member, Editorial Board, *Adv. Mater. Sci. Eng.,* 2012-present